Chemical Vapor Synthesis and Discovery of H$_2$ Storage Materials: Li-Al-Mg-N-H System

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University of Utah

THE UNIVERSITY OF UTAH

Project ID ST31

Overview

Timeline

- Start – March 2005
- Finish – March 2010
- Percent complete – 60%

Budget

- Total project funding

  DOE share: ~$800K

  Contractor share: $200K

- Funding received for FY07: $150K

- Funding for FY08: $150K
  (+$150K for PCT)

Barriers

- Reversible hydrogen content not sufficient (MYPP Barrier A),

- Inadequate kinetic properties (MYPP Barrier B)

- Desorption T's too high (MYPP Barrier (MYPP Barrier B)

Partners

- JPL, CalTech, GE, UNR, U Hawaii, SNL, SRNL, ORNL, U Pitt, CMU, Georgia Tech, Intematix,

- Project Lead: U of Utah 2

Objectives

Overall

- Discover new solid hydrides that meet reversibility and kinetics requirements
- Develop chemical vapor synthesis process (CVS) for production of nanosized solid metal hydrides
- Demonstrate the effectiveness and unique properties of nanosized solid hydride materials

FY07-08

- Understand reaction mechanisms of materials based on lithium alanates (destabilized by light metal amides), and LiMgN,
- Establish capability and quantify NH_3 co-production during dehydrogenation,
- Synthesize new materials using high-energy high-pressure reactive milling process,
- Synthesis of nano precursor and hydride powders using Chemical Vapor Synthesis (CVS) process.

Milestones

| Month/Year	Milestone or Go/No-Go Decision	Milestone Status
April - 06	Milestone: Complete design and set-up of the chemical vapor synthesis reactor systems and demonstrate their feasibility.	Achieved.
September - 08	Milestone: Demonstrate feasibility of selected materials (LiMgN and $Li_3AlH_6+3LiNH_2$)for hydrogen storage based on their capacity, reversibility, kinetics, and thermodynamic properties.	
September - 09	Go/No-Go Decision: Based on comprehensive characterizations of the thermodynamic and kinetic properties of LiMgN and $Li_3AlH_6+3LiNH_2$, Go/No-Go decisions on these two material systems will be made.	
September - 10	Milestone: Full report, conclusions, and recommendations on selected materials.	

Technical Approach

- Collaborate with MHCoE Theory Group to identify promising candidate materials (LiMgN)
- Exploit interactions between amides, alanates, and simple hydrides to discover new reactions / material systems,
- Use TGA, XRD, and FTIR as basic rapid screening tools, and NMR, in-situ XRD, and PCT for in-depth characterizations and understanding,
- Use high-pressure high-energy (HPHE) mechanochemical milling method to synthesize nanosized and non-equilibrium materials,
- Use Chemical Vapor Synthesis (CVS) process to produce nanosized precursor powders (e.g. Al, Li. Mg, LiMgN, MgB_2).

Accomplishments Highlights

1. Using PCT, confirmed that LiMgN is a **<u>reversible</u>** material with 6.6 wt. % or greater capacity, characterized reaction mechanisms with XRD, FTIR, NMR.

2. Elucidated the cycling mechanism for $Li_3AlH_6 + 3LiNH_2$

3. Identified the critical dependence of the regeneration of Li_3AlH_6 on the heating rate of hydrogenation process.

4. Developed and used pH-ion meter capability to quantify the concentrations of NH_3 during dehydrogenation.

5. Identified the role of heating rate in NH_3 release from hydrogenated LiMgN.

6. Conducted preliminary measurement of the reaction enthalpy of LiMgN.

7. Achieved improved desorption properties of $7MgH_2$/TiH system prepared by high pressure high energy milling.
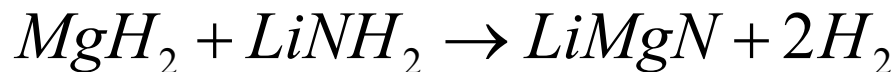
8. Made nanosized Al powder using CVS method.

Focus on 2 Promising Materials

I. Reactions of LiNH$_2$ with lithium alanate materials

$$Li_3AlH_6 + 3LiNH_2 \longleftrightarrow Al + 3Li_2NH + \frac{9}{2}H_2$$
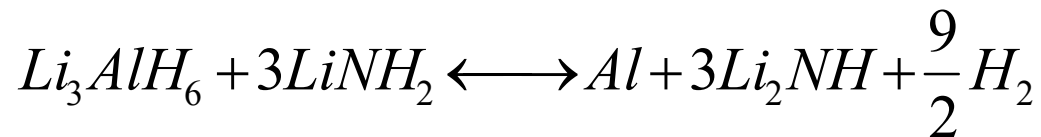
-- Expected to have theoretical hydrogen capacity in the 6-7 wt. % range, coupling known reactions…
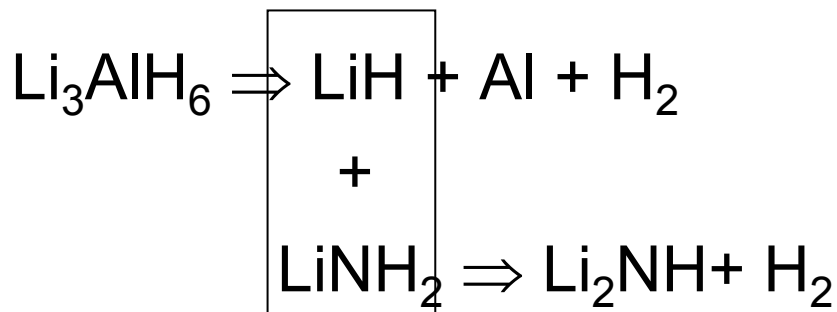
II. Reactions Leading to LiMgN

$$MgH_2 + LiNH_2 \rightarrow LiMgN + 2H_2$$

-- Theoretically predicted by MHCoE partners (Johnson, Sholl, Alpati) to have $\Delta H = 32kJ/molH_2$, with 8.2% theoretical hydrogen capacity.

Given that:

- Li_3AlH_6 decomposes to LiH and H_2
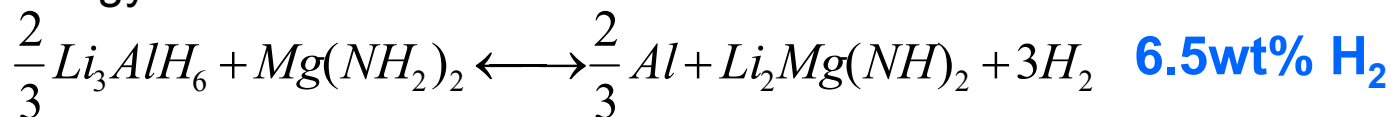- LiH releases H_2 when reacting with $LiNH_2$

1. Chen, J.; et al. *J. Phys. Chem.* **2001**, *17*, 1665
2. Chen, P.; et al. *Nature*, **2002**, *420*,320
3. Luo, W.; J. *Alloys Compd.*, **2004**, *381*, 284

Perhaps we can place a source of LiH (from Li_3AlH_6) in close proximity to $LiNH_2$ to get enhanced H_2 evolution:

$$Li_3AlH_6 \Rightarrow LiH + Al + H_2$$
$$+$$
$$LiNH_2 \Rightarrow Li_2NH + H_2$$

Anticipated Rxns (with amide in 2 forms):

$$Li_3AlH_6 + 3LiNH_2 \longleftrightarrow Al + 3Li_2NH + \frac{9}{2}H_2 \quad \textbf{7.2wt\% H}_2$$

or by analogy….

$$\frac{2}{3}Li_3AlH_6 + Mg(NH_2)_2 \longleftrightarrow \frac{2}{3}Al + Li_2Mg(NH)_2 + 3H_2 \quad \textbf{6.5wt\% H}_2$$

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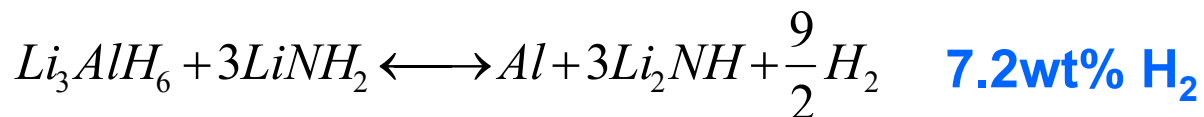
Basic reactions, capacity, and reversibility confirmed by TGA, XRD, PCT, and NMR analysis.
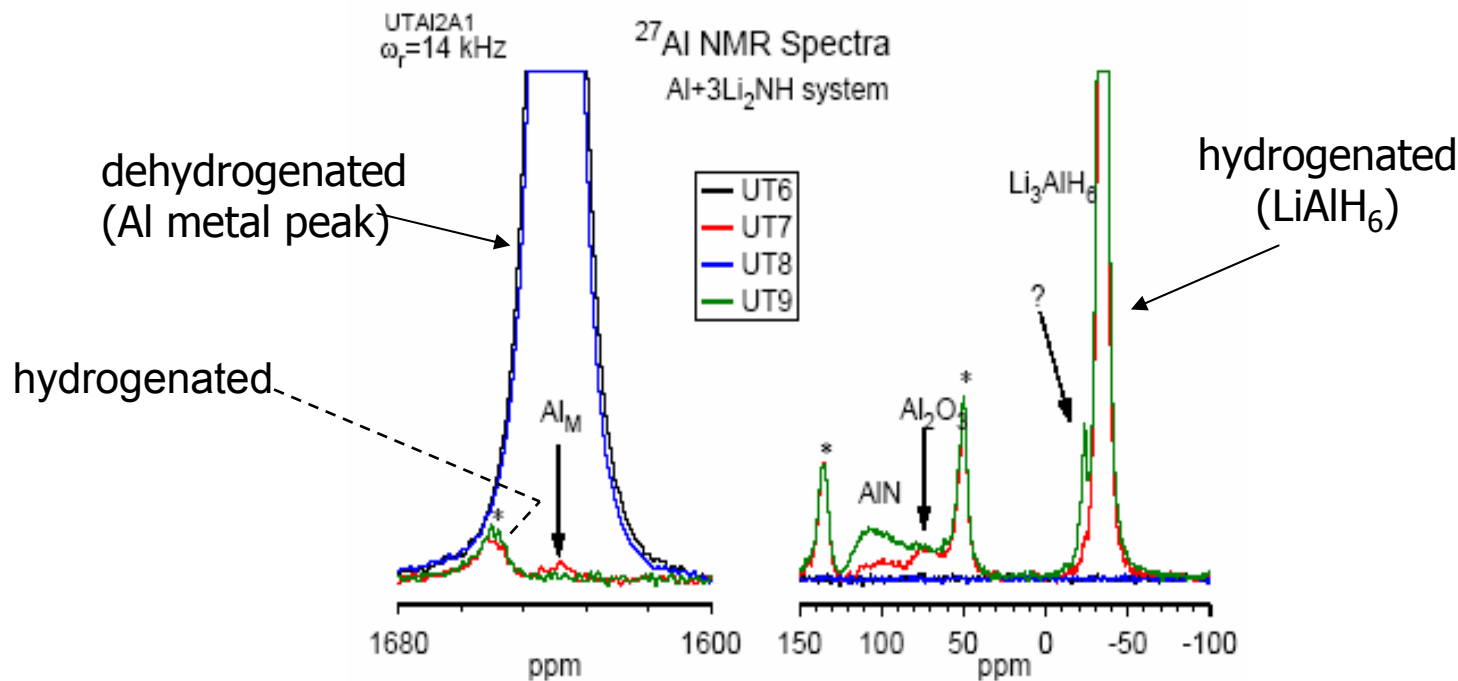
TGA of hydrogenated (138 bar, 300°C) sample.
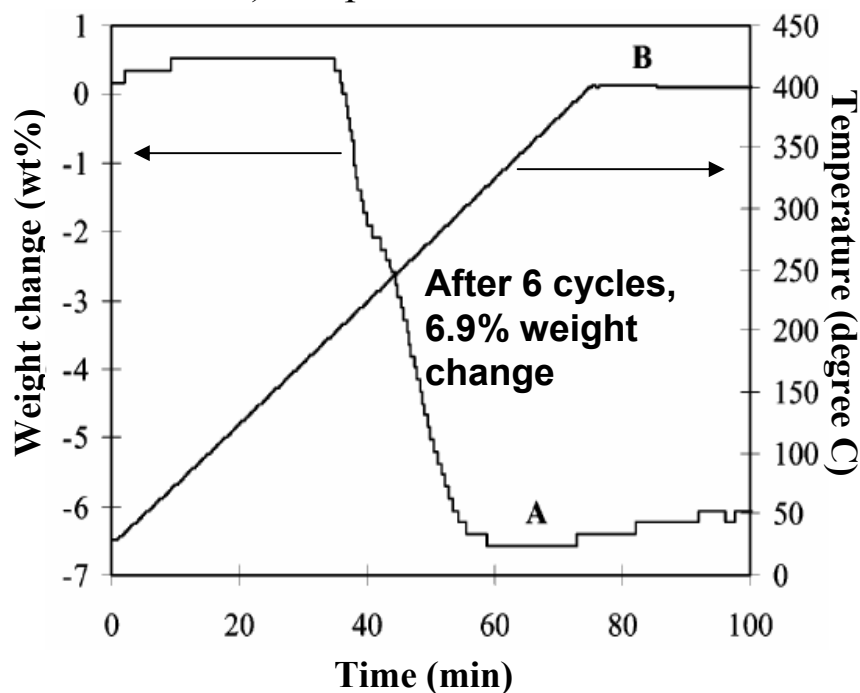
PCT of Li$_3$AlH$_6$/3LiNH$_2$/4wt%TiCl$_3$, T= 375 °C

After 6 cycles, 6.9% weight change

data by Karl Gross, Hy-Energy
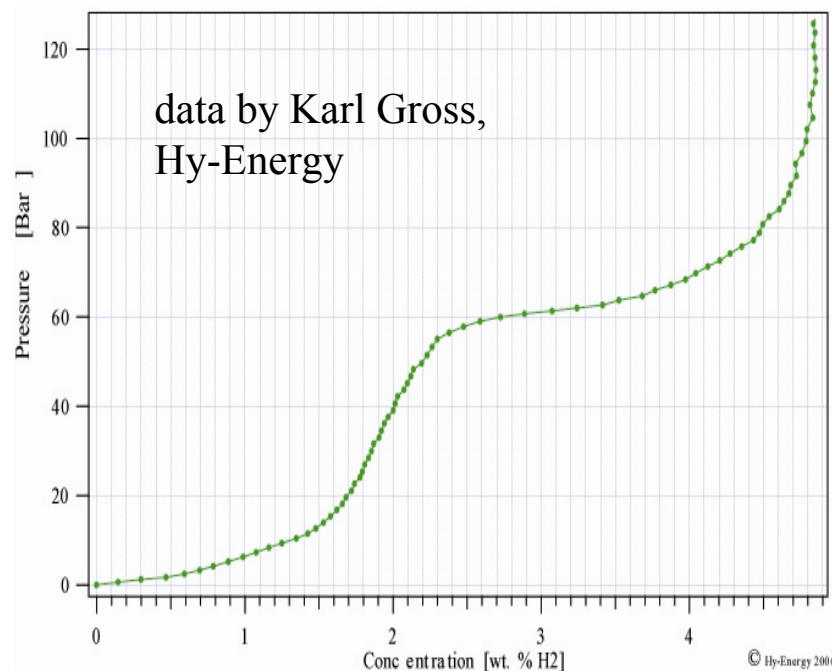
- Two plateau pressures at ~1 and 60 bar respectively.
- van't Hoff plot shows the material is less stable than MgH$_2$.

NMR confirms AlH$_6$ ⟷ Al conversion

Characterization of Li$_3$AlH$_6$+3LiNH$_2$ (Bowman, Hwang):

> ➤ ^{27}Al NMR results prove that the system shows stable cycling behavior:
> Al+3Li$_2$NH + 9/2H$_2$ ⟺ Li$_3$AlH$_6$ + 3LiNH$_2$
> ➤ ^{27}Al NMR: identifies Al(M), Li$_3$AlH$_6$, AlN (small), Al$_2$O$_3$ (small)
> ➤ There is unknown species found in ^{27}Al NMR of hydrogenated UT9 at -23.7 ppm, while the AlN was increased noticeably as the ads/des cycle was performed

Rehydrogenation Depends on Heating Rate

Hydrogenating Al + Li_2NH (the dehydrogenated product): Hydrogenating using heating rates of 1, 2, 5 and 10 °C/min at P = 172 bar H_2
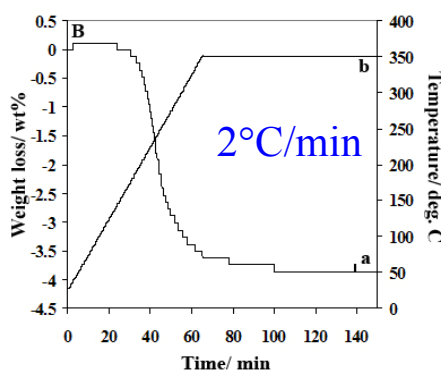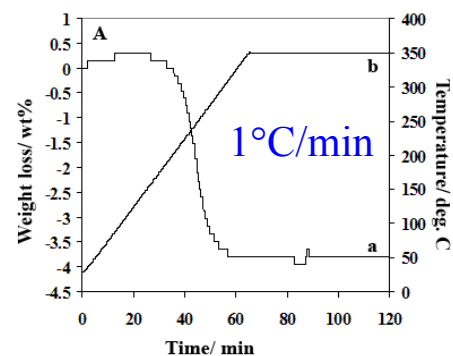
Slower hydrogenation heating rate yields only ~ 4 wt. % material, no characteristic Li_3AlH_6 peak in XRD.
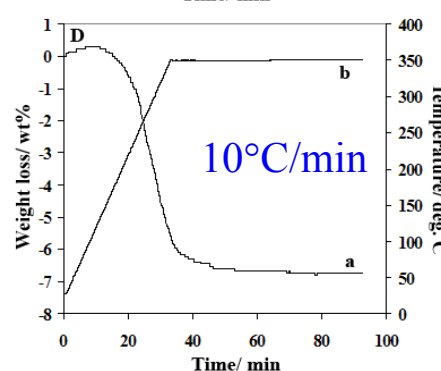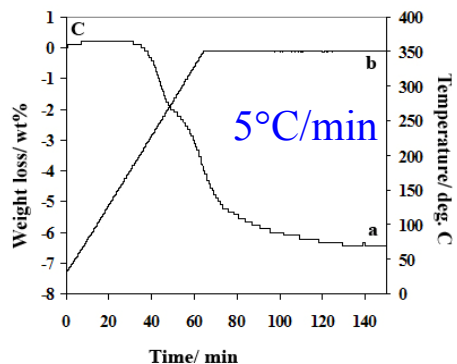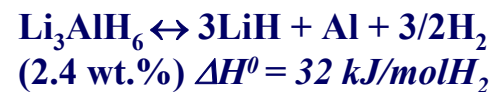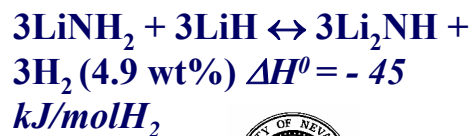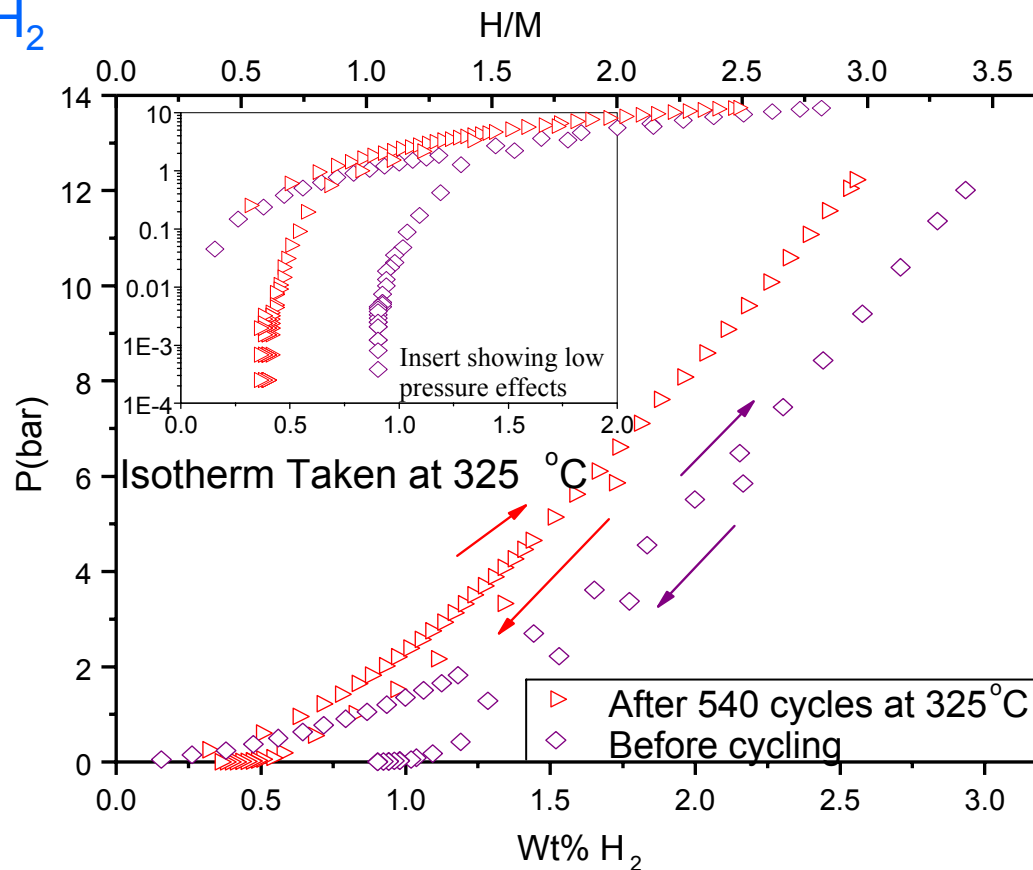
Faster hydrogenation heat rate yields ~ 6.9 wt. % material, XRD shows Li_3AlH_6

The heating rate needs to be higher than 5 °C/min and the reaction temperature needs to be greater than 220 °C in order to make the reversible conversion. Results confirmed by ^{27}Al and [6]Li NMR studies.

(Li$_3$AlH$_6$+3LiNH$_2$) Stable with Cycling and Modest O$_2$ Exposure

Start with ball-milled Li$_3$AlH$_6$/3LiNH$_2$

- Isotherm taken before and after 540 cycles shows a small loss in H$_2$ capacity (~0.6%) using 100 ppm O$_2$ in UHP hydrogen.

- **Therefore, material loss by volatilization (NH$_3$) is a negligible problem for this material under the conditions of this study.**

- Note that cycling LiNH$_2$ + LiH ↔ Li$_2$NH + H$_2$ in Industrial hydrogen (with no Li Alanate) showed ~2.6% hydrogen loss after 500 cycles under similar cycling conditions

Isotherm Taken at 325 ^{o}C

Insert showing low pressure effects

Legend:
- ▷ After 540 cycles at 325°C
- ◇ Before cycling

Axes: H/M (top), P(bar) (left), Wt% H$_2$ (bottom)

3LiNH$_2$ + 3LiH ↔ 3Li$_2$NH + 3H$_2$ (4.9 wt%) $\Delta H^0 = -45$ kJ/molH$_2$

Li$_3$AlH$_6$ ↔ 3LiH + Al + 3/2H$_2$ (2.4 wt.%) $\Delta H^0 = 32$ kJ/molH$_2$

Dhanesh Chandra

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New Candidate Material - LiMgN

A theoretically predicted reaction by MHCoE theorists (Alapati, Johnson, Sholl, et.al*):

$$MgH_2 + LiNH_2 \rightarrow LiMgN + 2H_2 \quad \Delta H = 32 kJ/mol\ H_2$$

Carnegie Mellon

GeorgiaInstitute of **Tech**nology

Potential Advantages:

➢ all the hydrogen in MgH_2 and $LiNH_2$ could be released (theoretical 8.2%)

➢ by-passes the undesirable imide ($Li_2Mg(NH)_2$) which forms when the MgH_2:$LiNH_2$ ratio is 2:1**

Questions:

➢ Does the rxn proceed?
➢ Is it reversible?

*. Alapati, S.V.; Johnson, K.J., Sholl, D.S. *J.Phys.Chem.*, **2006**, *110*, 8769

. Luo, W.; J. *Alloys Compd.*, **2004, *381*, 284
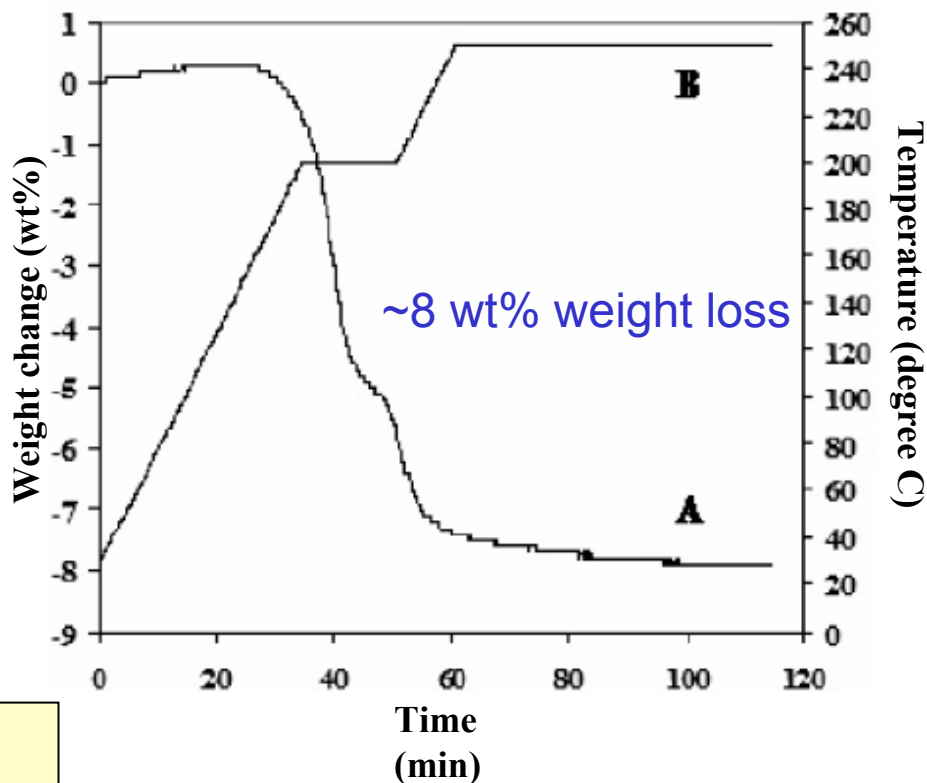
TGA Data: first, hydrogenate Ti-doped LiMgN, then desorb….

Rehydrogenation
conditions:

Pressure: 2000 psi H_2

Temperature: 160 °C

Holding time: 6 hours
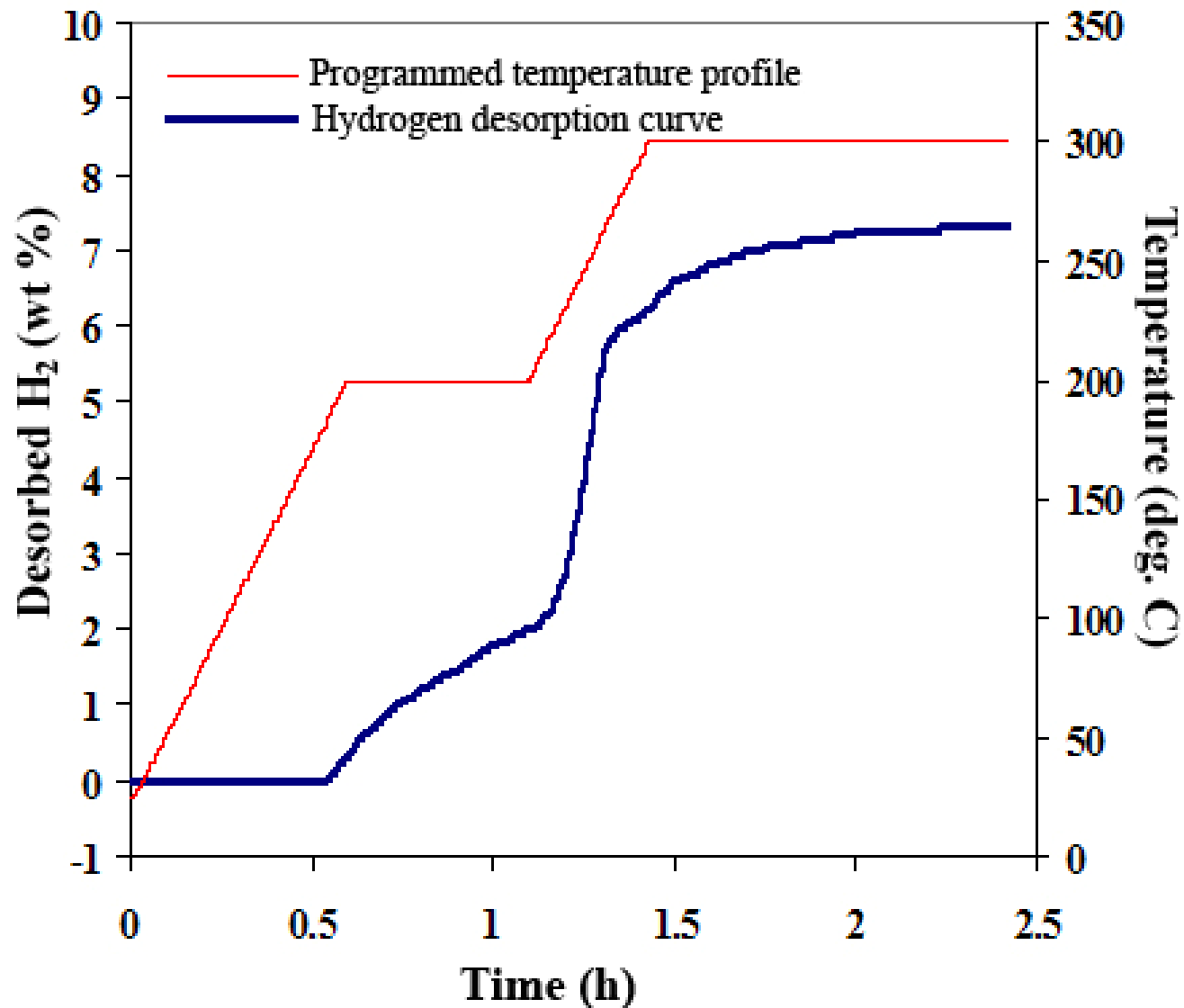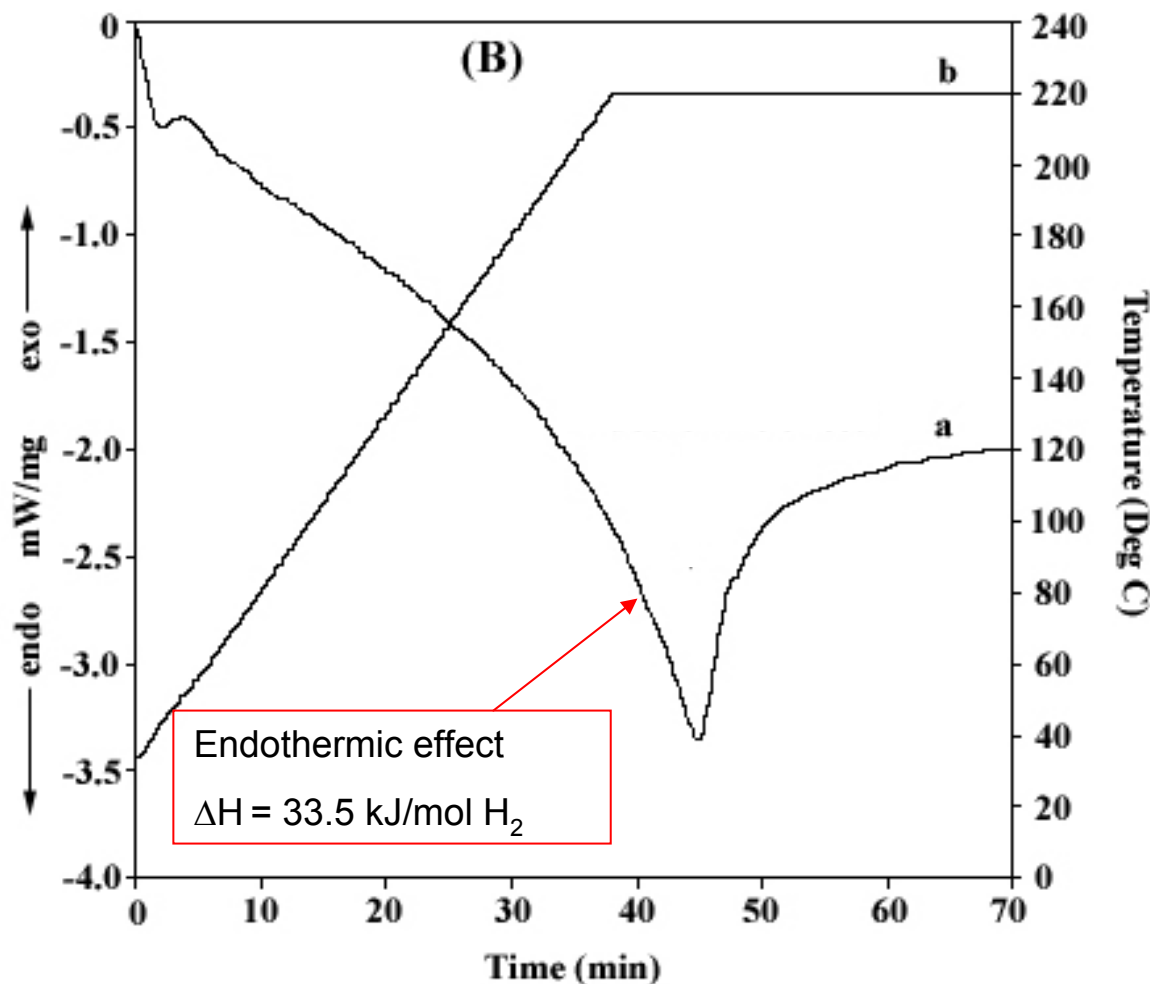
TGA of rehydrogenated TiCl$_3$-doped LiMgN

~8 wt% weight loss

B

A

Time
(min)

Weight change (wt%)

Temperature (degree C)

LiMgN can be hydrogenated
at temperatures below 240 °C

TPD for LiNH$_2$+MgH$_2$ after jar-roll milling for 48 hours

Measuring ΔH of the dehydrogenation reaction of $LiNH_2+MgH_2$

DTA curve of the dehydrogenation reaction of $LiNH_2+MgH_2=LiMgN+2H_2$


Endothermic effect

ΔH = 33.5 kJ/mol H_2

- ➢ One reaction step detected during the dehydrogenation of $LiNH_2+MgH_2$

- ➢ The ΔH value for the reaction is 33.5 kJ/mol H_2, which is close to the theoretically predicted reaction enthalpy of 29.7 (31.9) kJ/ mol H_2 reported by Alapati[1] et al using the USPP (PAW) approach.
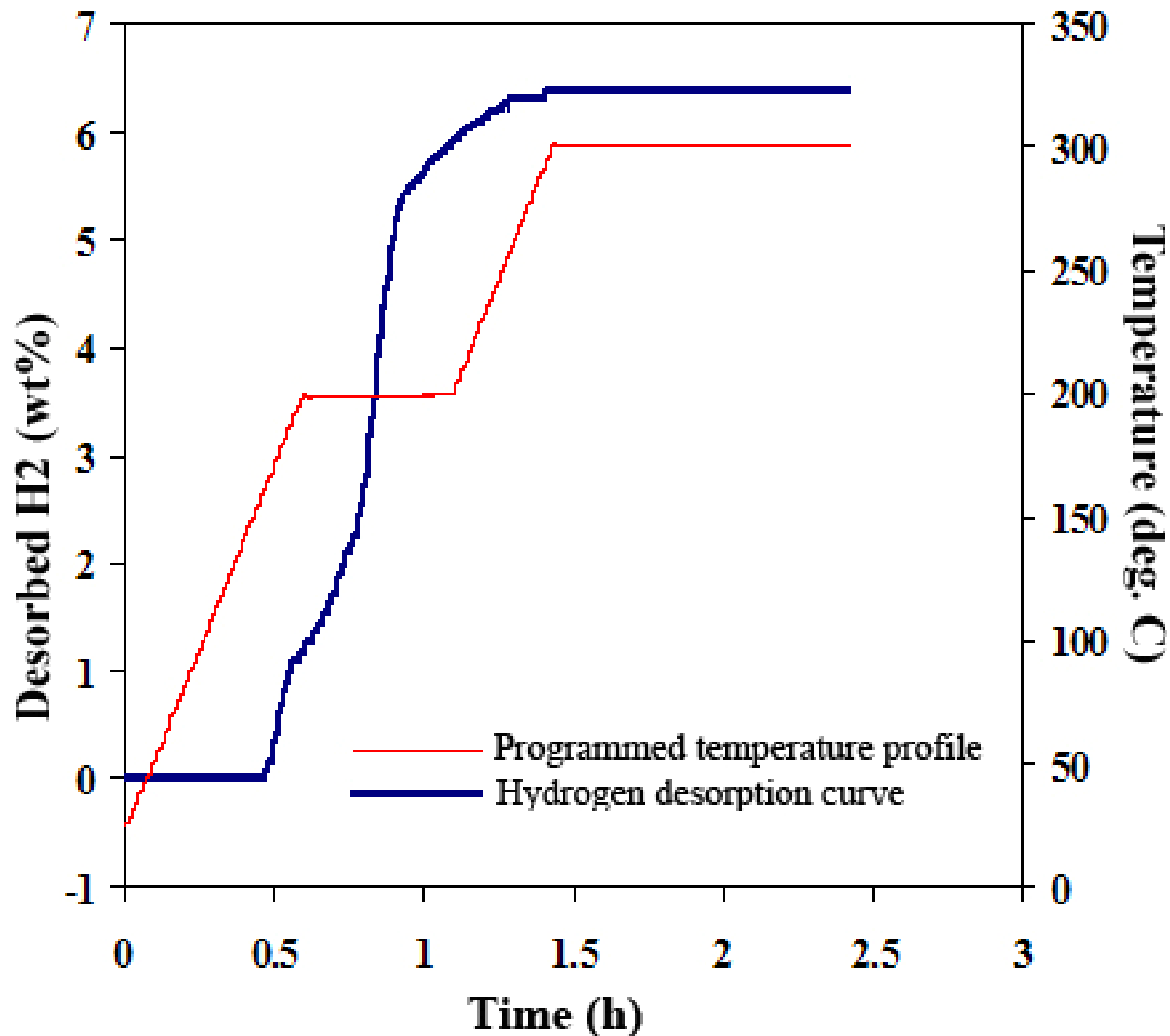
1. Alapati, S. V.; Johnson, K. J.; Sholl, D. S. *J. Phys. Chem. B* **2006**, *110*, 8769.
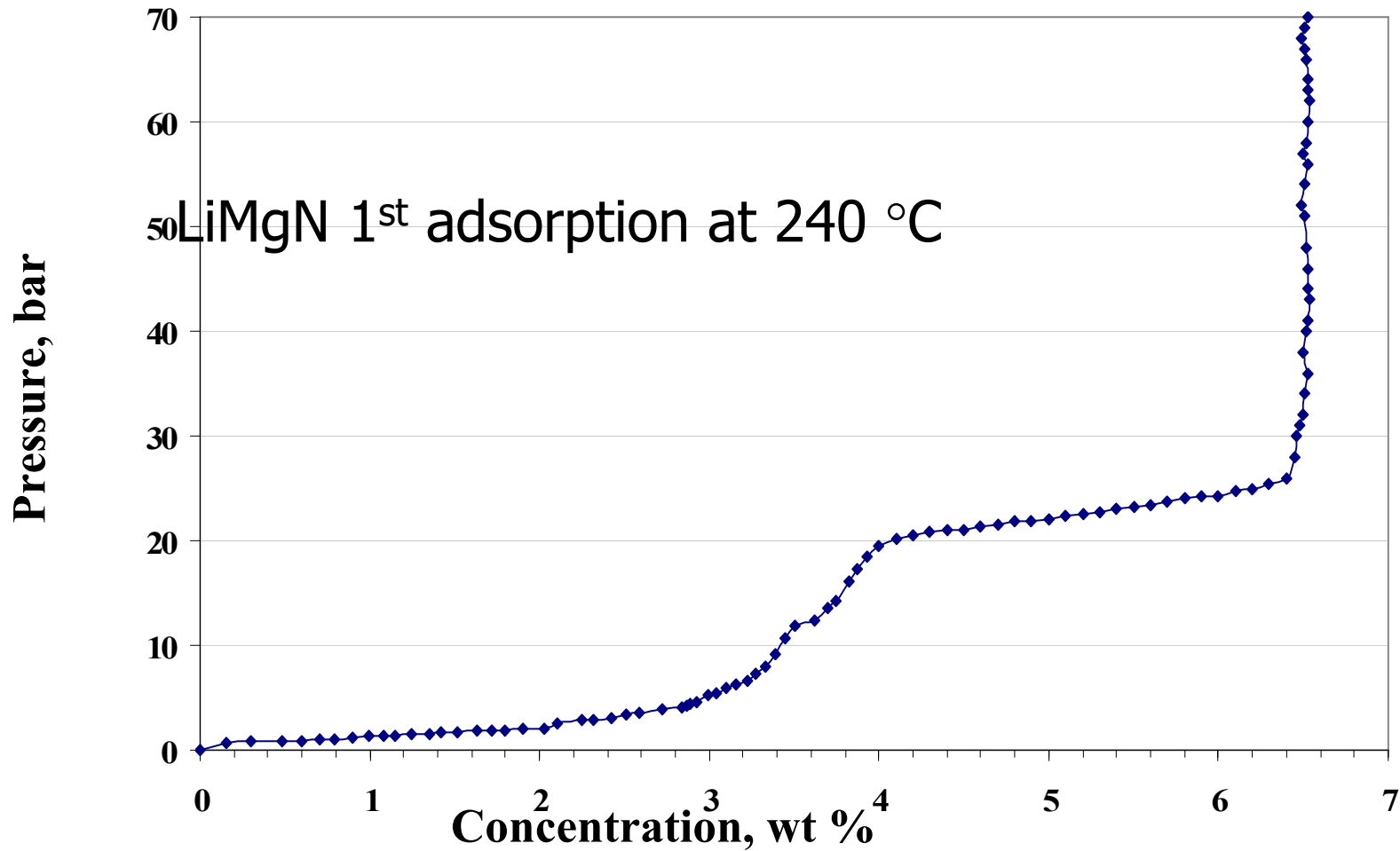
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TPA of LiMgN: H_2 pressure 140 bar. 6.8 wt% of H_2 pick-up. Note that ~2 wt% of H_2 is adsorbed at the room temperature (further study needed).

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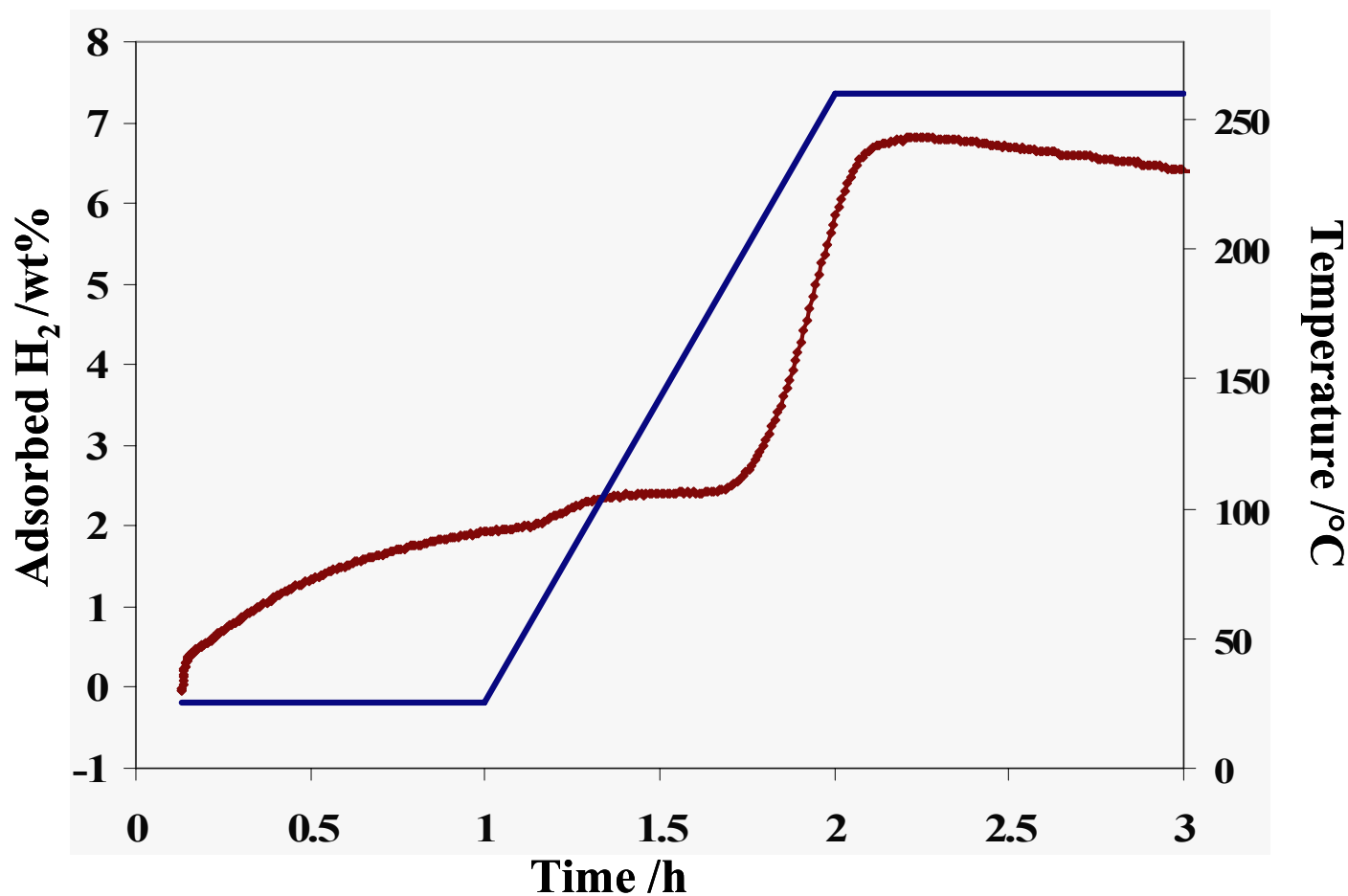
TPD for LiMgN after 1st hydrogenation at 172 bar and 240 °C for 10 hours

LiMgN 1st adsorption at 240 °C
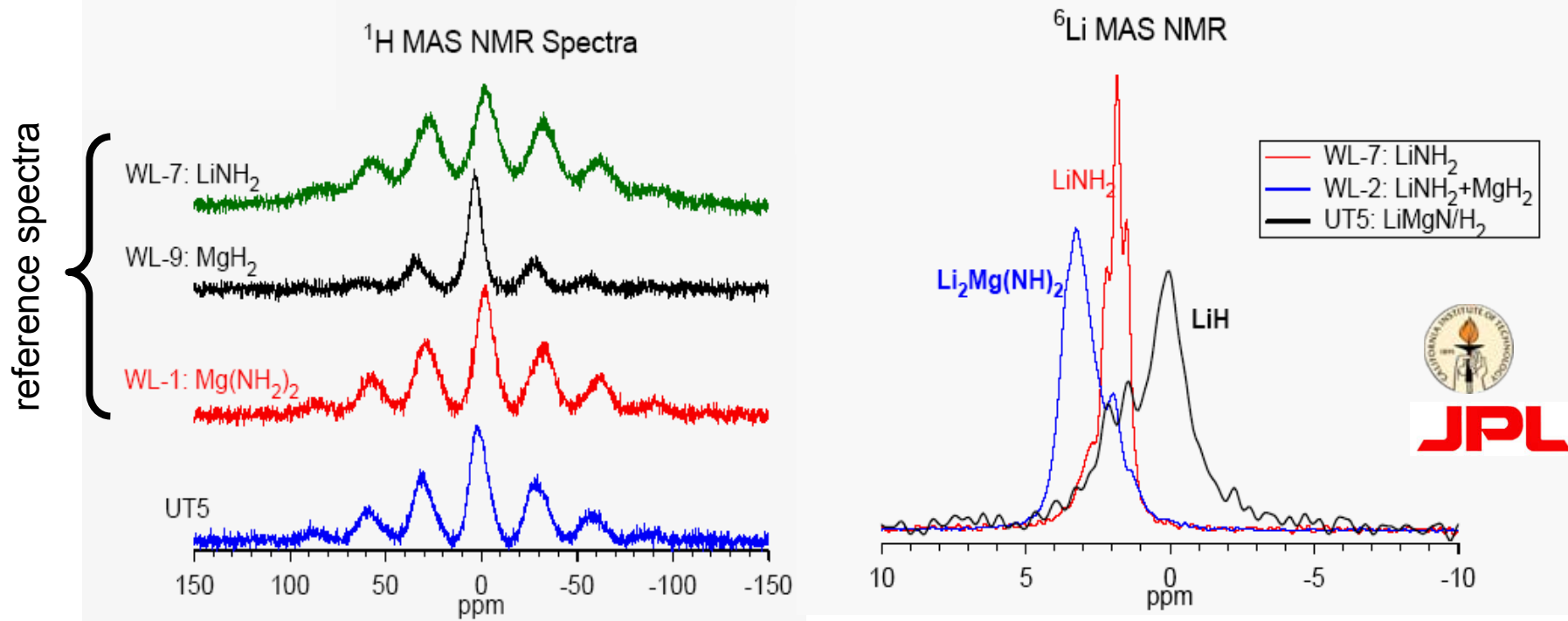
Isothermal Re-hydriding of LiMgN (Anton)

Cycle MgH2:LiNH2 (4%TiCl3)
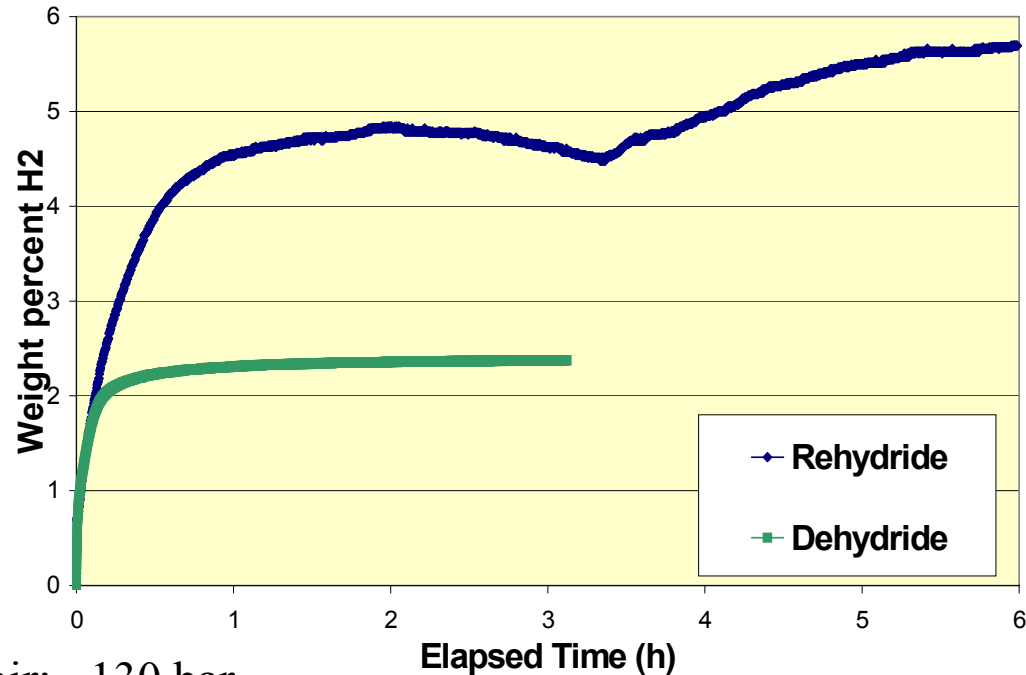
- Nominal pressure of reservoir: ~130 bar
- wt% rehydrided: ~ 5.7
- Staring material: dehydrided sample at 280 °C
- Possible 2-step rehydriding reaction in the process of being characterized. To be verified in additional experiments.
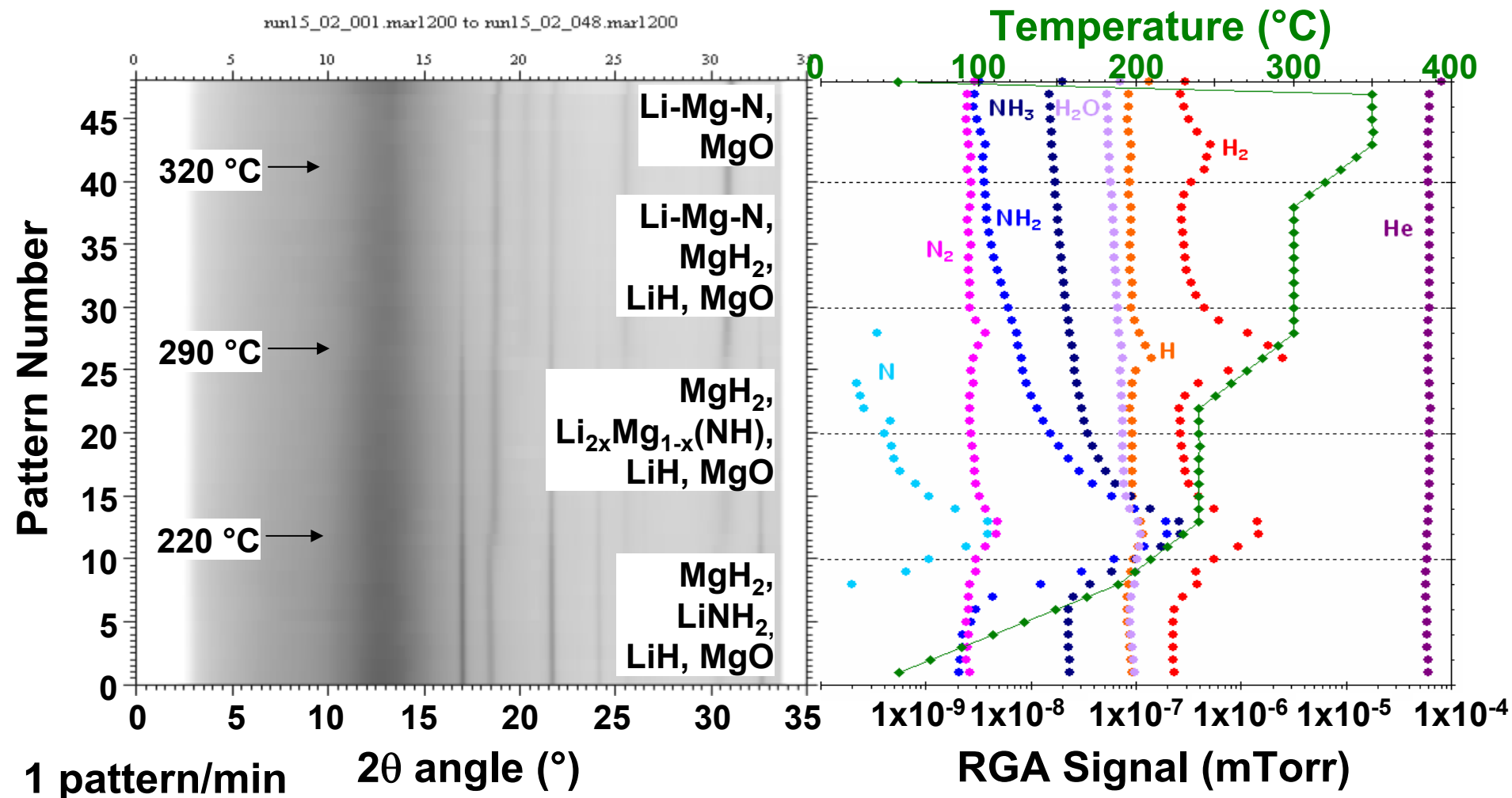
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Hydrogenated LiMgN Products Probed by NMR

UT5: LiMgN after hydrogenation at 138 bar and 240 °C NMR by Bowman, Hwang

Hydrogenated LiMgN: ^{1}H is inconclusive (maybe MgH_2 + $LiNH_2$) while ^{6}Li shows LiH + $LiNH_2$.

LiMgN hydrogenation rxn pathways are complex

Temperature (°C)

RGA Signal (mTorr)

2θ angle (°)

1 pattern/min

Pattern labels (left panel):
- Li-Mg-N, MgO
- Li-Mg-N, MgH$_2$, LiH, MgO
- MgH$_2$, Li$_{2x}$Mg$_{1-x}$(NH), LiH, MgO
- MgH$_2$, LiNH$_2$, LiH, MgO

320 °C → 290 °C → 220 °C →

RGA labels: NH$_3$, H$_2$O, NH$_2$, N$_2$, N, H$_2$, H, He

hydrogenated $-LiMgN \xrightarrow{\Delta} Li_{2x}Mg_{1-x}(NH)_2 + MgH_2 \xrightarrow{\Delta} LiMgN$
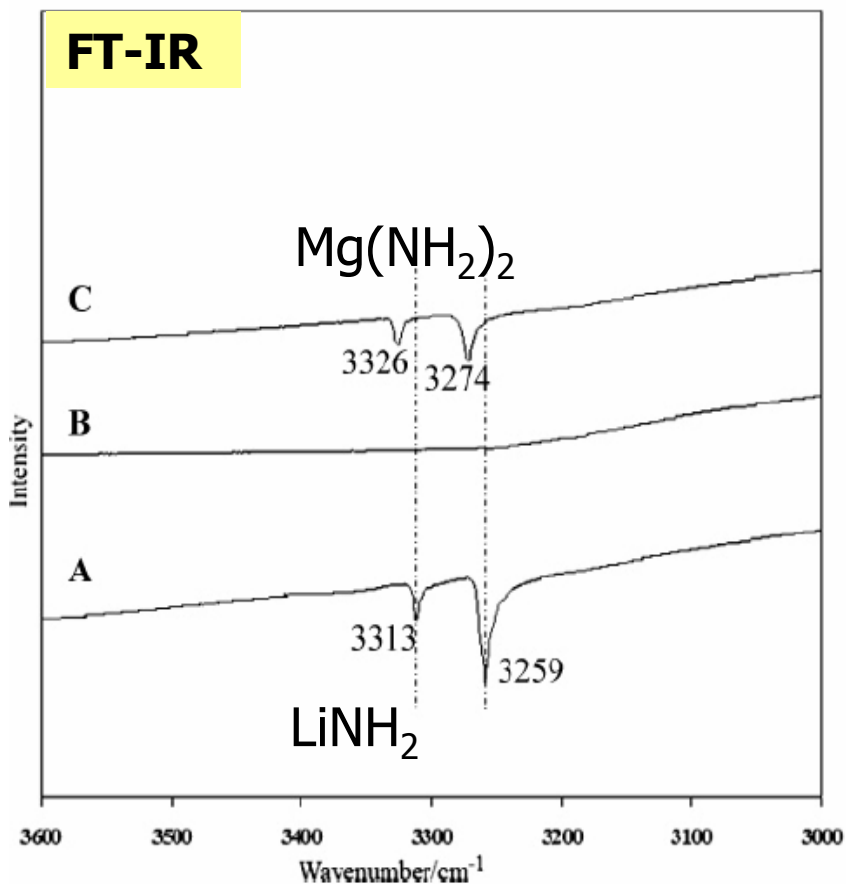
22

Hydrogenated/Dehydrogenated LiMgN Probed by XRD
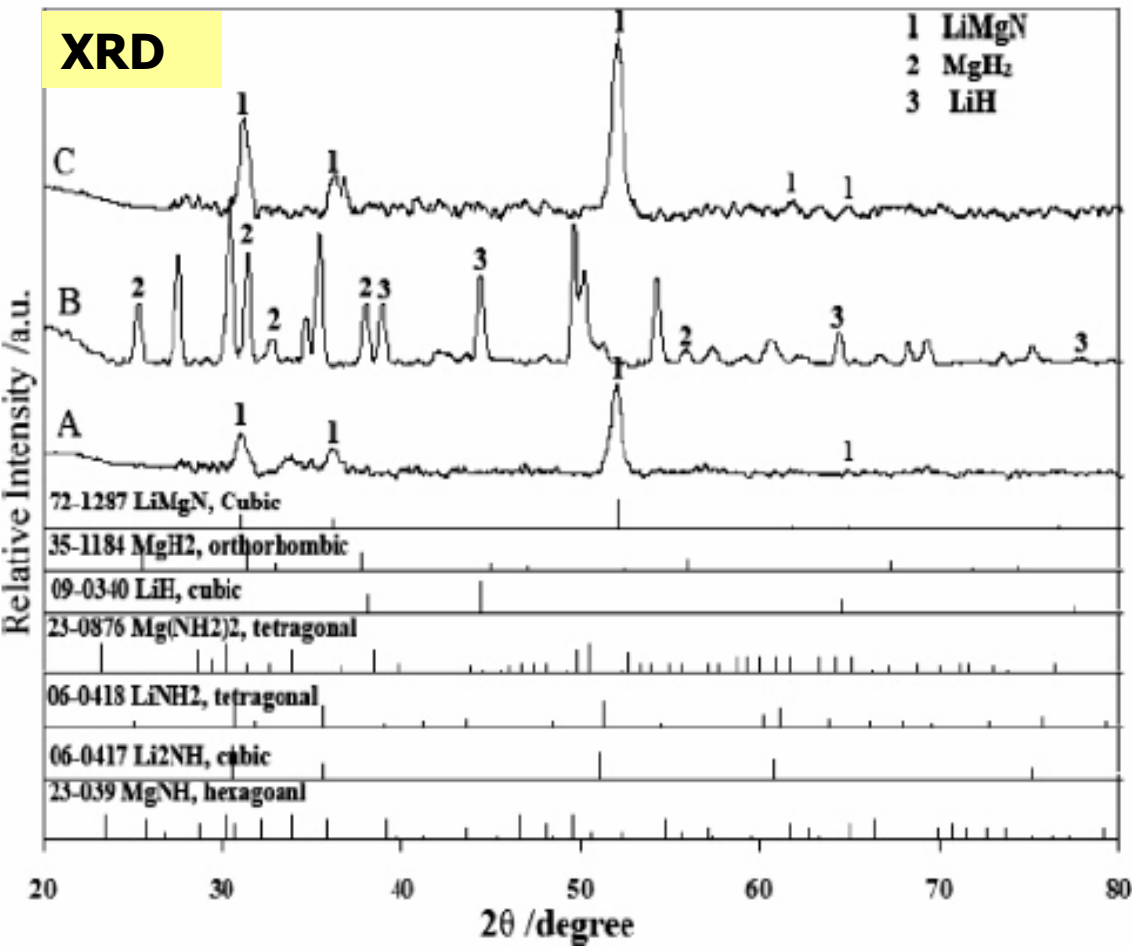
A) TiCl$_3$-doped LiMgN
B) TiCl$_3$-doped LiMgN after hydrogenation.
C) Dehydrogenation products of hydrogenated TiCl$_3$-doped LiMgN

> ➤ MgH$_2$ and LiH are formed in the hydrogenation process.
>
> ➤ LiMgN reformed after a hydrogenation and dehydrogenation cycle

Cycled LiMgN Probed by FTIR

FT-IR

A) $TiCl_3$-doped $LiNH_2$+MgH_2 (starting mat.)
B) LiMgN
C) LiMgN after hydrogenation

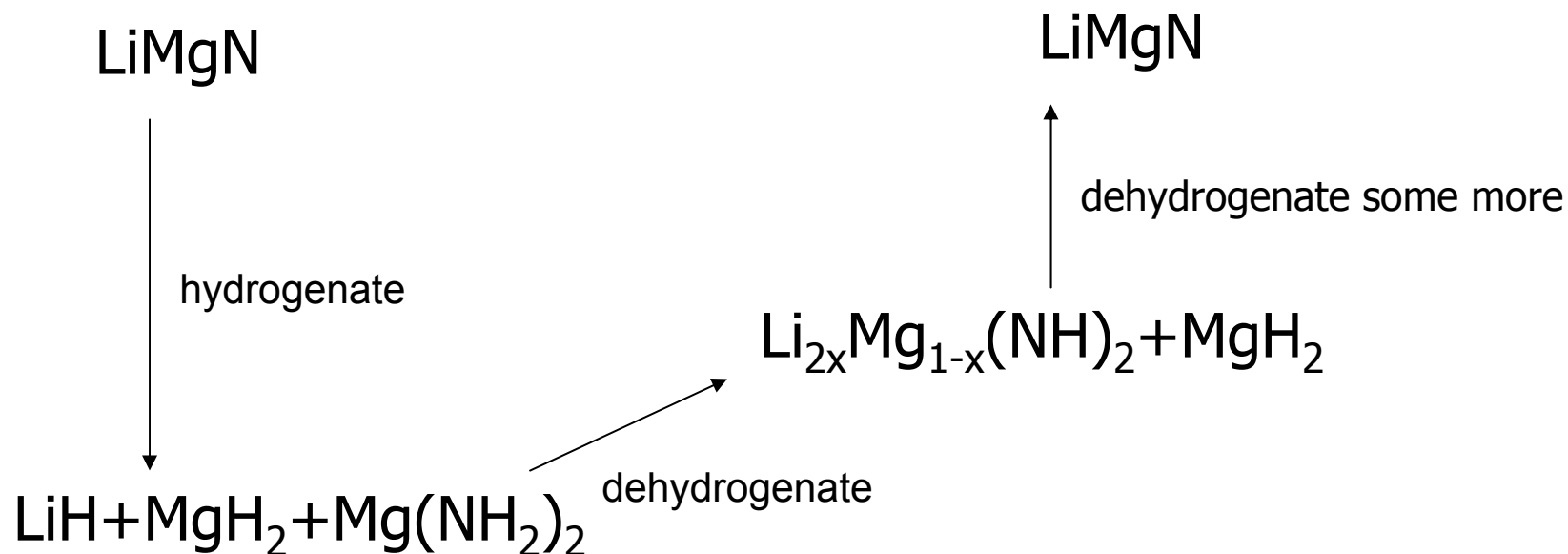FTIR results showed:

$Mg(NH_2)_2$ is formed in the hydrogenation process.

Measuring ΔH of the dehydrogenation reactions of hydrogenated-LiMgN

DTA curve of the dehydrogenation reaction of hydrogenated-LiMgN

Endothermic effect

$\Delta H_2 = 23.56$ kJ/mol H_2

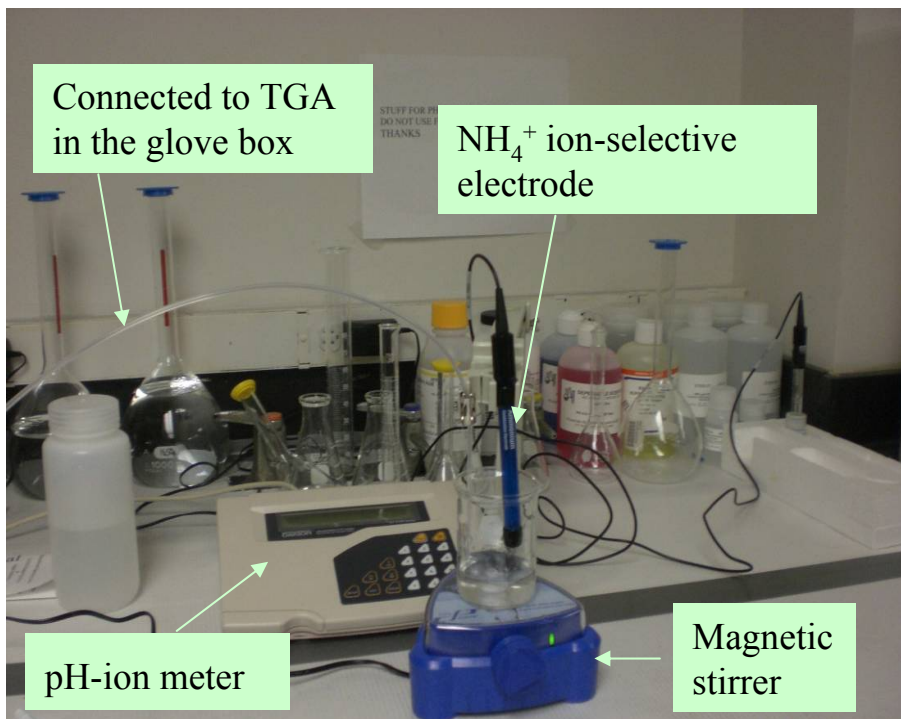Endothermic effect

$\Delta H_1 = 15.35$ kJ/mol H_2
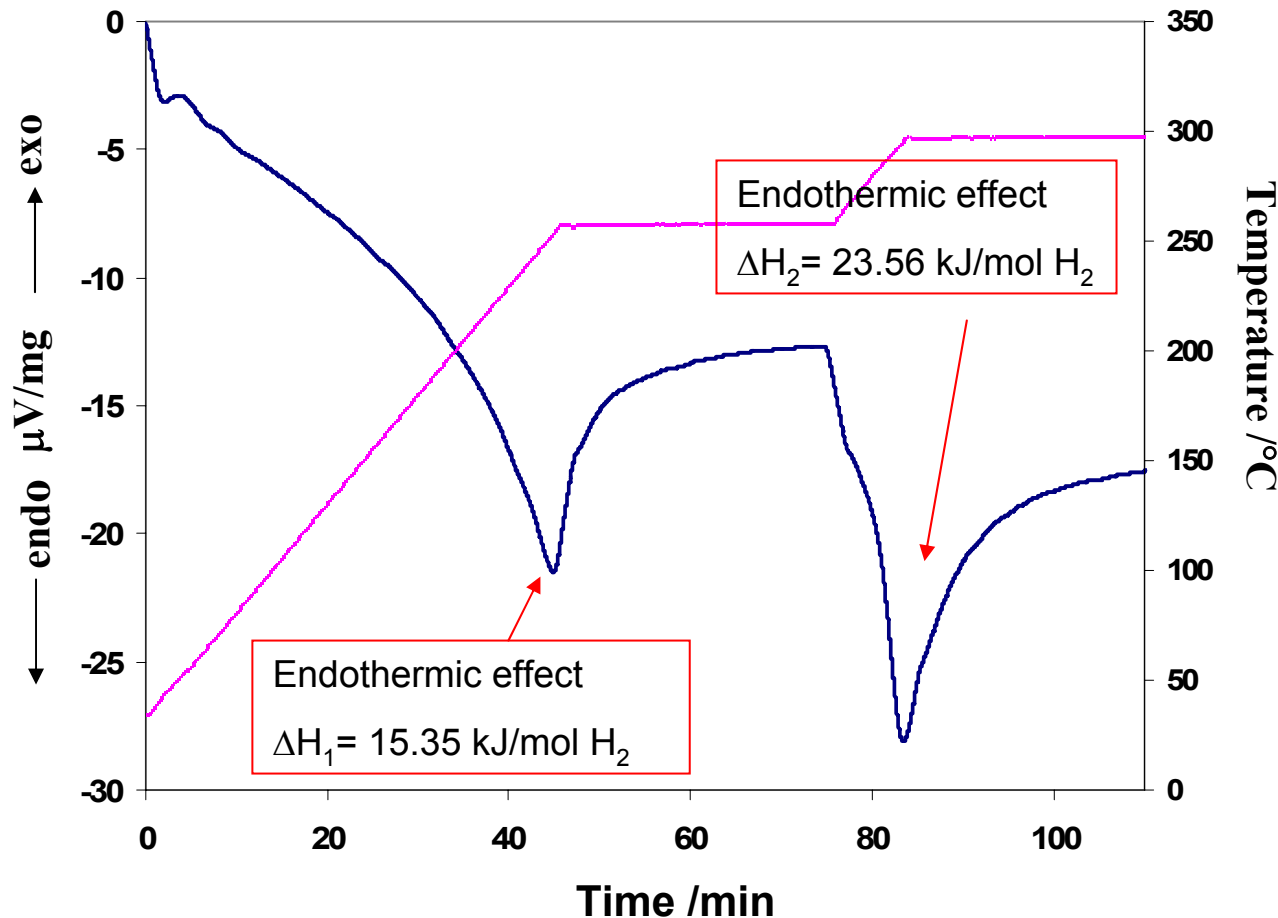
- ➢ Two reaction steps detected during the dehydrogenation of the hydrogenated LiMgN sample

- ➢ The ΔH values for the two reactions are 15.35 and 23.56 KJ/mol H2 respectively.

Proposed Reaction Scheme for LiMgN

LiMgN

LiMgN

$\downarrow$ hydrogenate

dehydrogenate some more $\uparrow$

$Li_{2x}Mg_{1-x}(NH)_2 + MgH_2$

$LiH + MgH_2 + Mg(NH_2)_2$ dehydrogenate

Proposed reaction pathway based on XRD, FTIR and in-situ XRD results to date. Results in partial agreement with theoretical expectations

Connected to TGA in the glove box

NH$_4^+$ ion-selective electrode

pH-ion meter

Magnetic stirrer

The gas products from the system can be carried to an acid solution by inert gas (Ar). If NH$_3$ is formed during the dehydrogenation process, the acid solution can catch all the NH$_3$ gas to convert to NH$_4^+$. Then the pH-ion meter can measure the NH$_4^+$ concentration via a NH$_4^+$ ion-selective electrode.

## Measuring NH$_3$ using pH-ion meter connected to TGA:

- pH-ion meter measures the changes of pH value of the solution

- The pH-ion meter is calibrated by 3-point calibration using the standard pH buffers (4, 7, 10) before any measurements.

- When the gas containing NH$_3$ is fed into the solution, NH$_3$ reacts with H$^+$ to form NH$_4^+$, which changes the pH value.

- The concentration of NH$_4^+$ is measured based on the changes in pH values.

-- the instrument was calibrated by measuring NH$_3$ release from LiNH$_2$, combined with TGA measurements
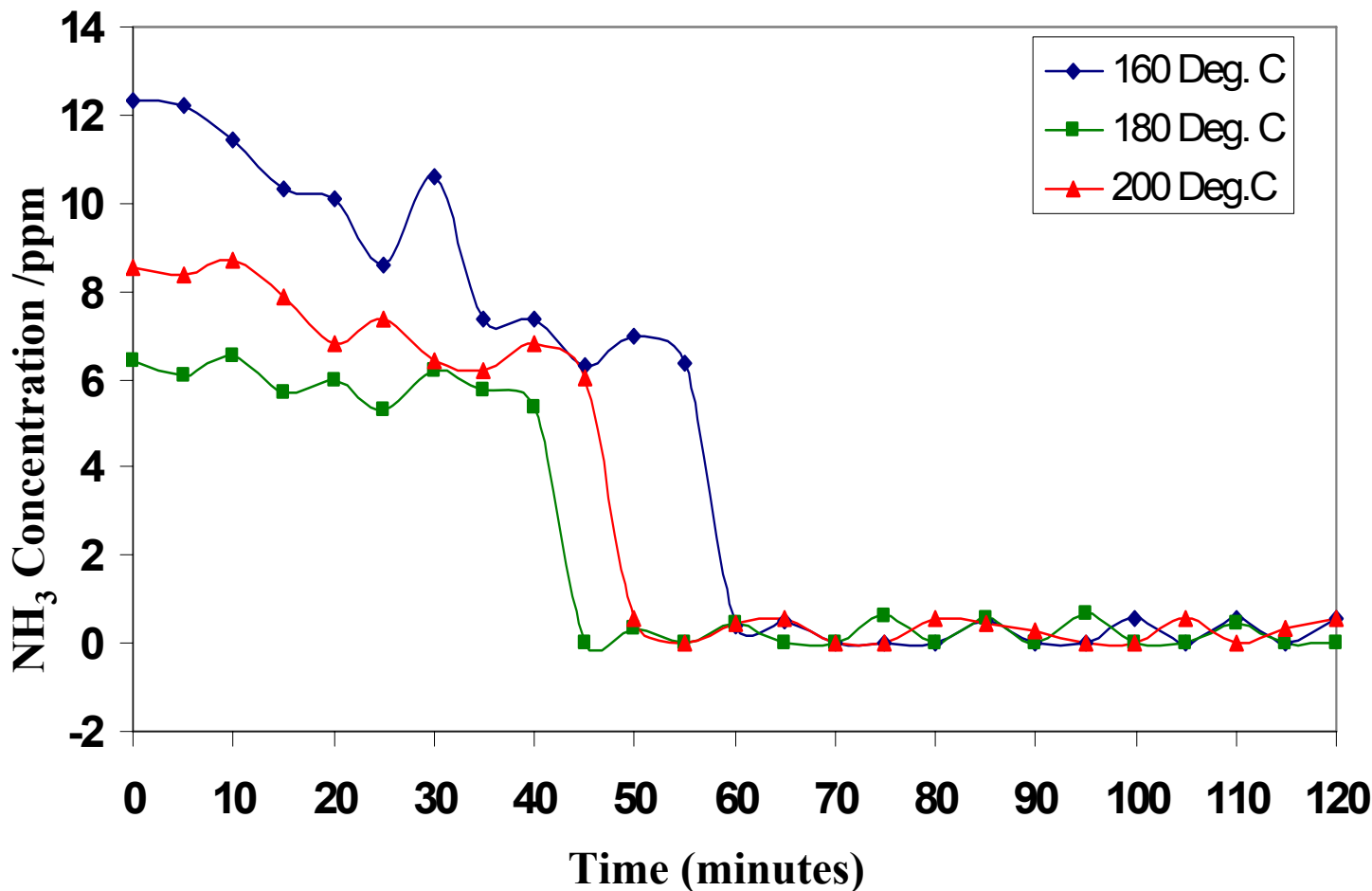
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Measuring NH$_3$ concentration

NH$_3$ concentration during dehydrogenation of the hydrogenated-LiMgN as a function of the temperature. The heating rate is 5 °C/min.
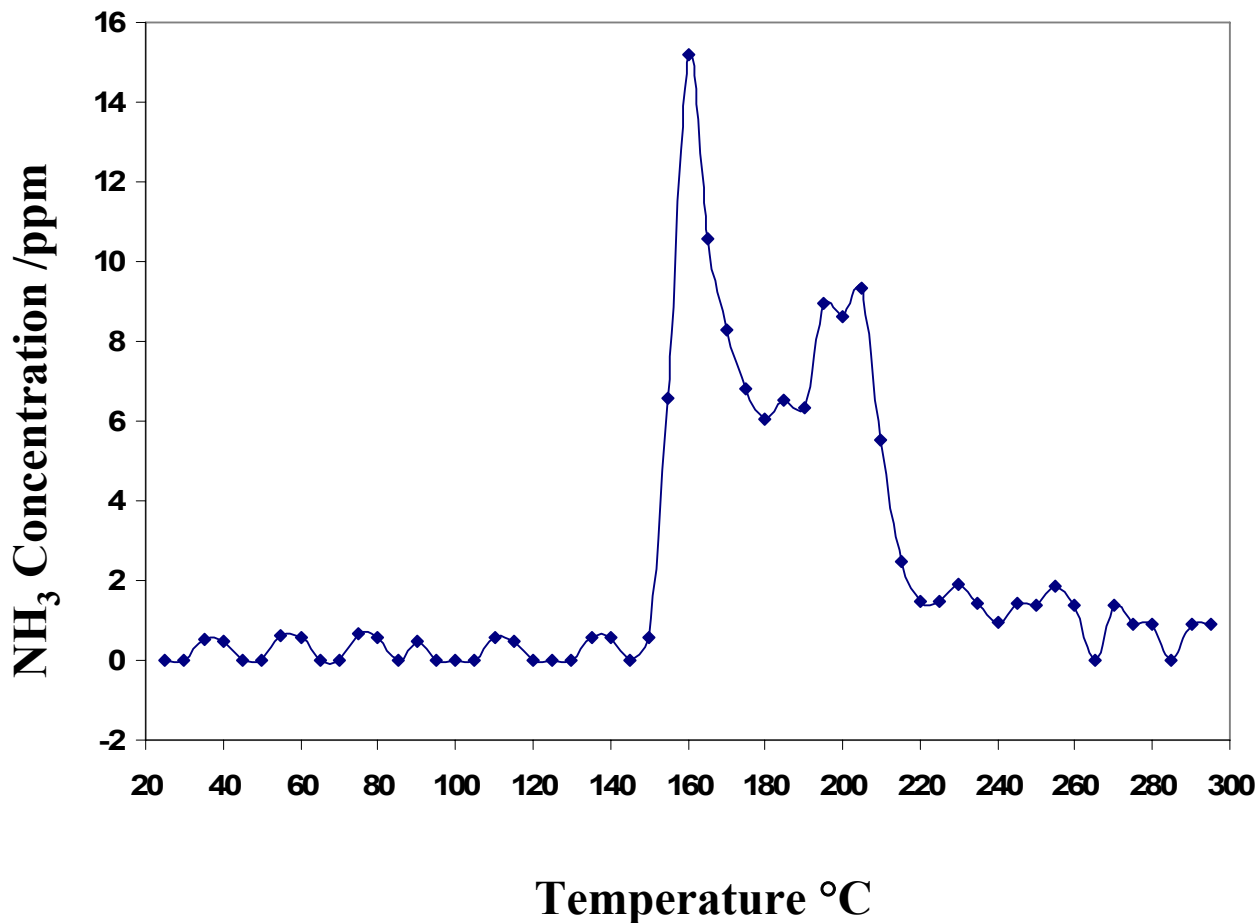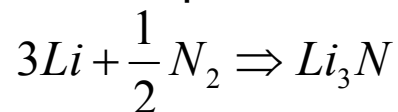
Measuring NH$_3$ concentration

NH$_3$ concentration as a function of time during isothermal dehydrogenation of the hydrogenated-LiMgN. The heating rate prior to isothermal holding is 5 °C/min.
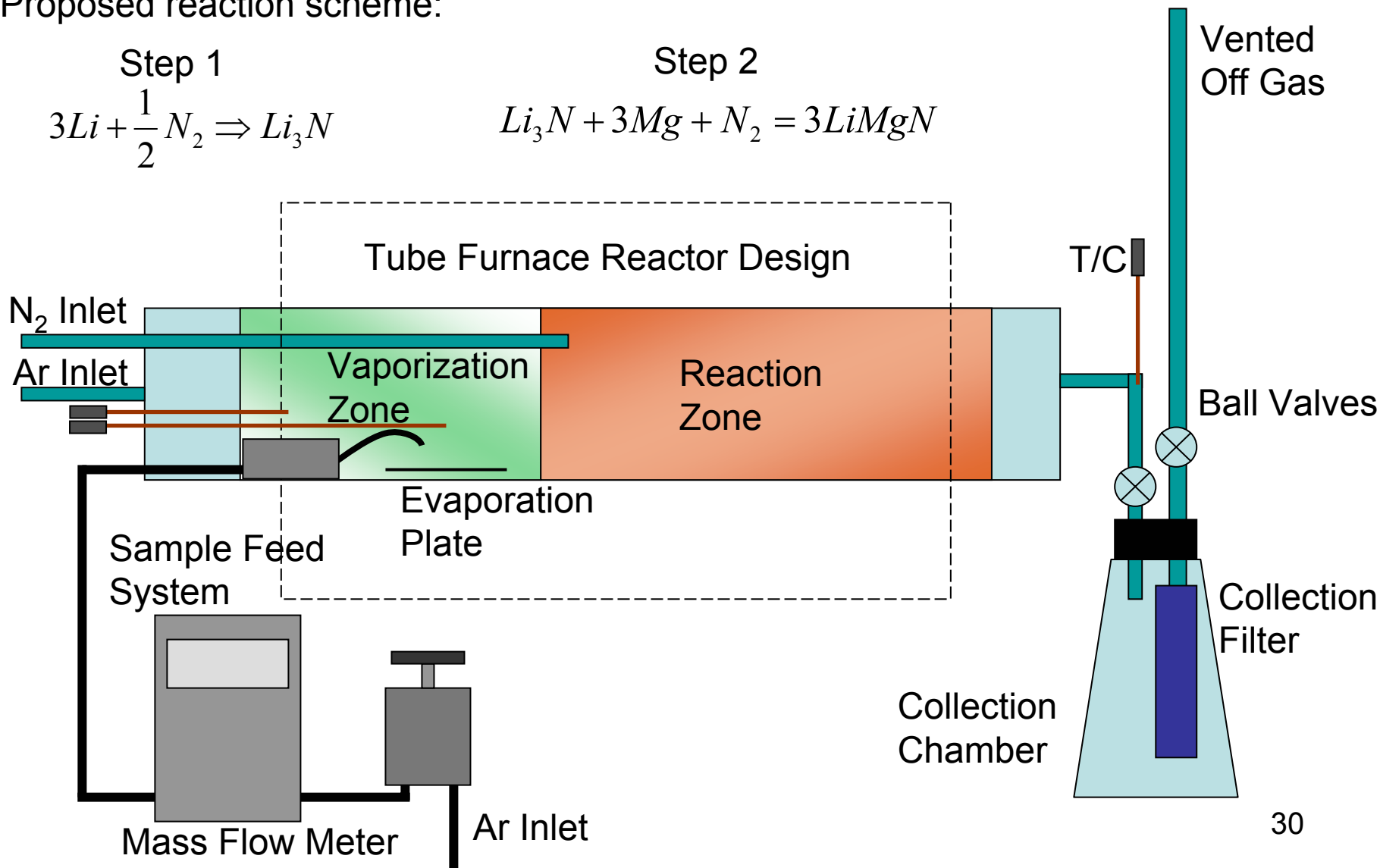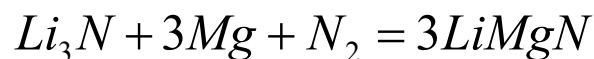
Chemical vapor synthesis of LiMgN

Proposed reaction scheme:

Step 1

$$3Li + \frac{1}{2}N_2 \Rightarrow Li_3N$$

Step 2

$$Li_3N + 3Mg + N_2 = 3LiMgN$$

Vented Off Gas

Tube Furnace Reactor Design

N$_2$ Inlet

Ar Inlet

T/C

Vaporization Zone

Reaction Zone

Ball Valves

Evaporation Plate

Sample Feed System

Collection Filter

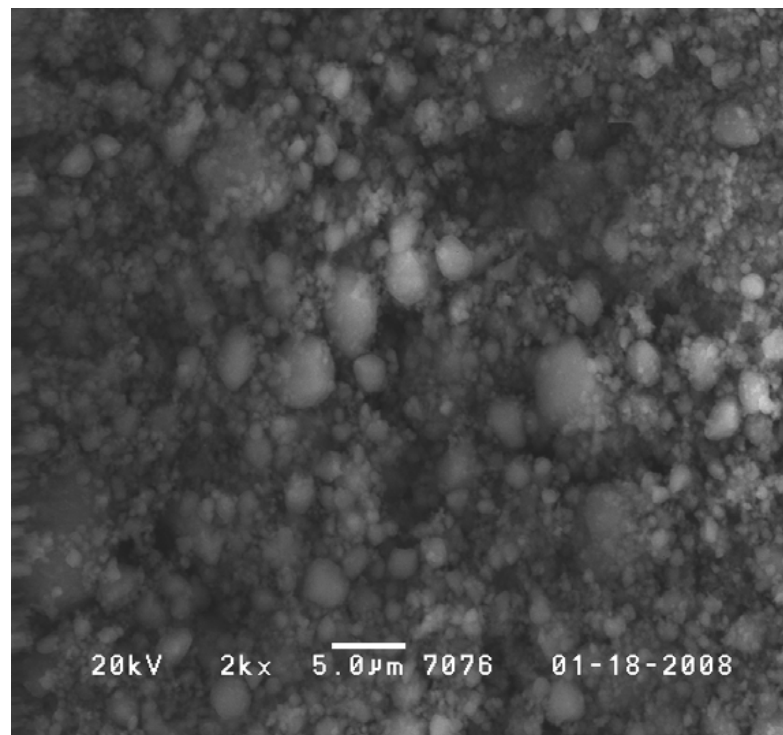Collection Chamber

Mass Flow Meter

Ar Inlet

Chemical vapor synthesis of LiMgN

Ultrafine LiMgN powders made by CVS process was successfully hydrogenated/dehydrogenated.
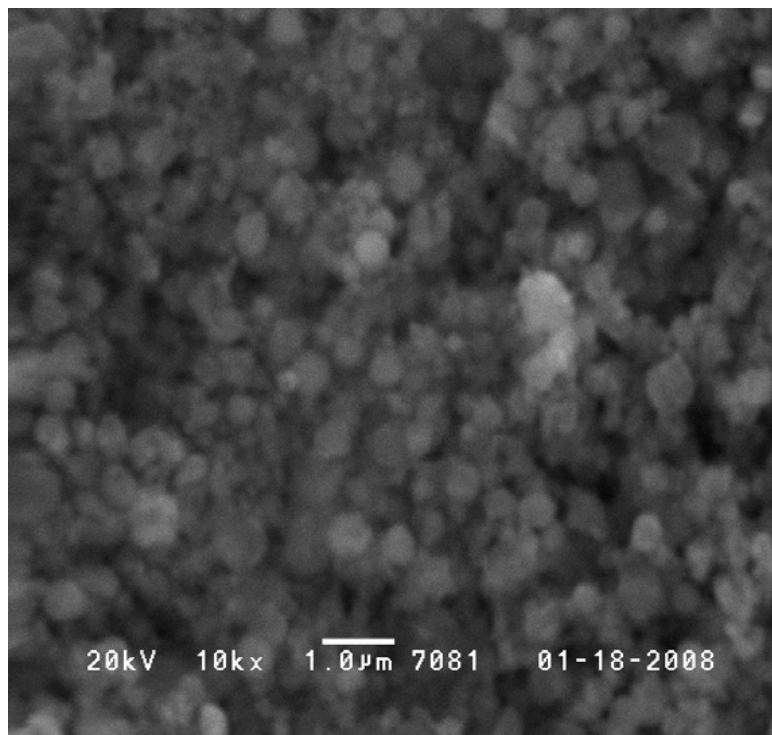
(a). CVS Powder Hydrogenated



(b). $LiNH_2 + MgH_2$ Ball Milled 96 hours

CVS produces LiMgN with more uniform sized particles than that of ball milling.
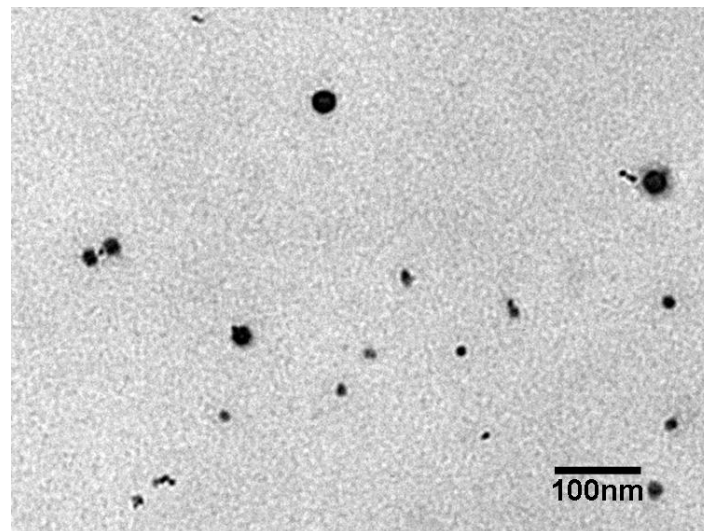
CVS synthesis of nanosized Al powder

- To support MHCOE partners' efforts to regenerate AlH_3,
- Modified the reactor from last year by controlling the residence time of the gas phase to reduce particle size,
- The average size of the produced powder is < 50 nm.

Nanosized Al powder was successfully produced

XRD Result
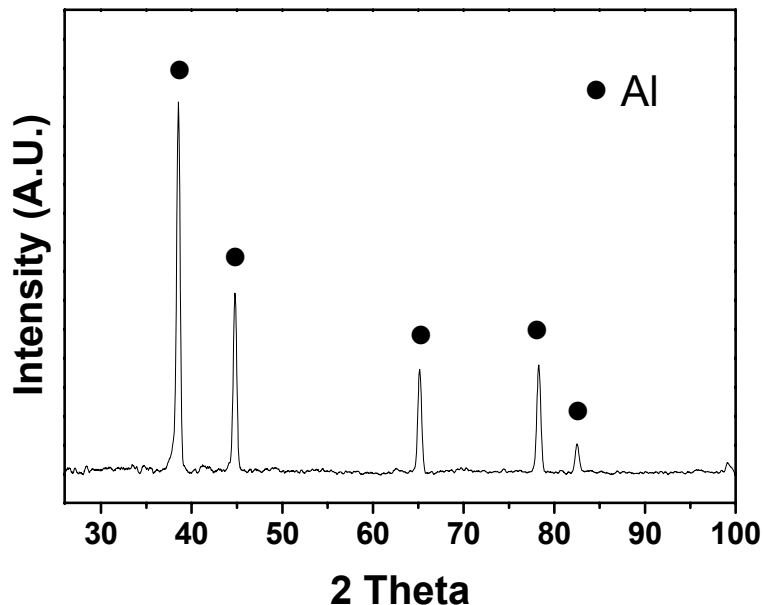
TEM Micrograph

100nm

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➢ $Mg_y Ti_{(1-y)} H$ thin film was found to store hydrogen reversibly with better kinetic properties compared to that of MgH_2.

Reference: P. Vermeulen, R.A.H. Niessen, P.H.L. Notten, "Hydrogen storage in metastable MgyTi(1-y) thin films", Electrochem. Commun. 8 (2006) 27-32.

➢ Challenge: synthesize this compound in powder form and maintain reversibility

➢ High-energy high-pressure (HEHP) mechanochemical approach was employed: mixtures $xMgH_2$+$yTiH_2$ were high-energy milled under 2000 psi H_2 pressure.

HPHE Milling Reactor 33
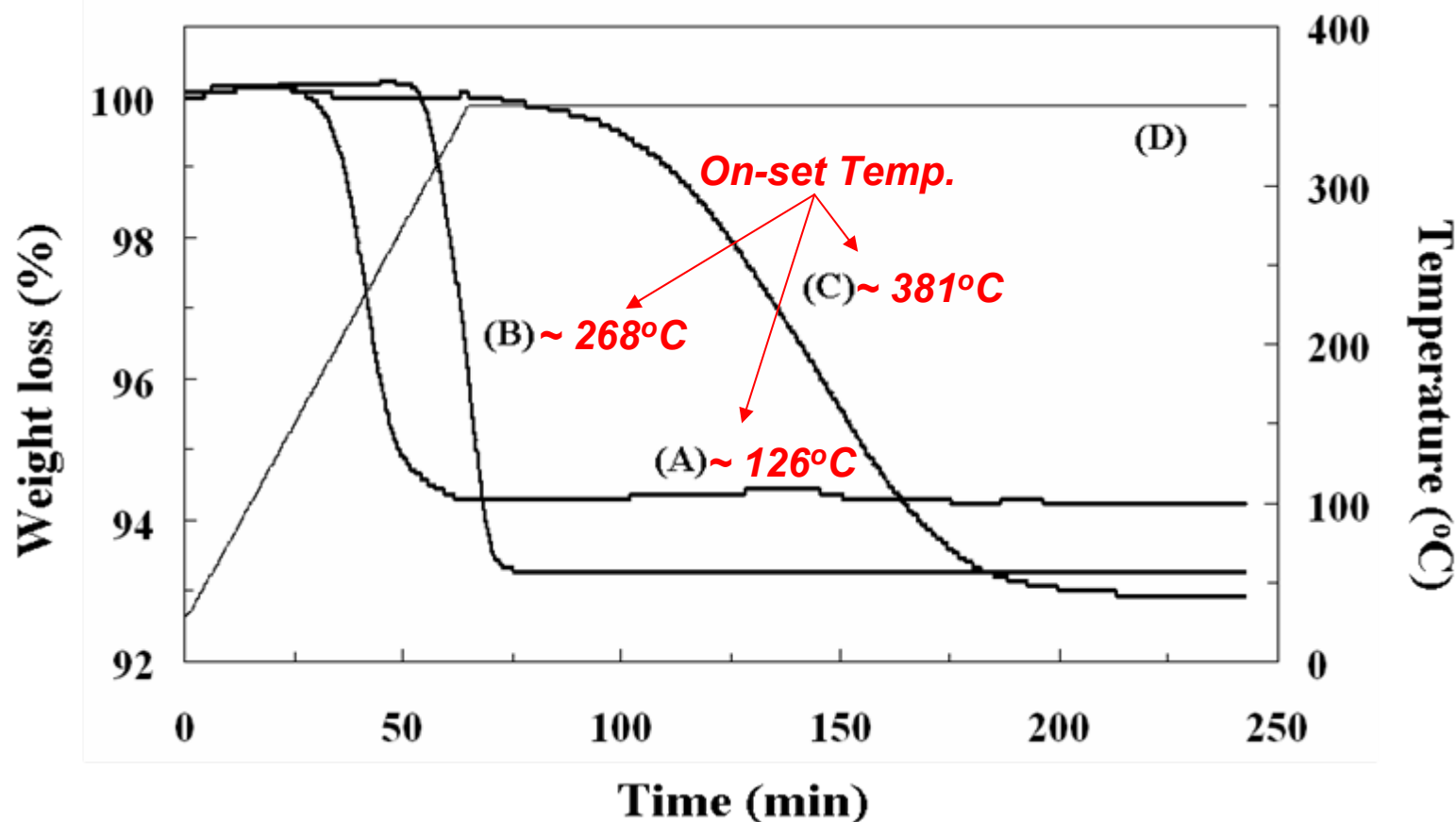
TGA curves of (A) milled 7MgH$_2$ - TiH$_2$ (B) milled MgH$_2$ (C) as-received MgH$_2$ (D) temperature profile for (A), (B), (C).

Summary

- LiMgN found to be reversible at moderate temperatures, a promising material that will be investigated further.

- The reversible reaction of $Li_3AlH_6/3LiNH_2$ was found to depend strongly on heating rate due to competing reactions and relative product stabilities.

- The co-generation of NH_3 during dehydrogenation of hydrogenated LiMgN is quantified, preliminary data is now available.

- CVS is a proven approach for synthesizing nanosized or ultrafine powders for hydrogen storage applications.

- The high pressure high energy mechanochemical method is once again demonstrated as a unique approach for making non-equilibrium materials.

Where the Amides Stand

Properties	Selected reversible hydrogen storage material systems						
	$MgH_2/$ Ni^{nano}	$NaAlH_4$	$2LiH/$ $LiNH_2$	$MgH_2/$ $2LiNH_2$	Li_3AlH_6 $/3LiNH_2$	$2/3Li_3AlH_6$ $/Mg(NH_2)_2$	LiMgN
Theoretical reversible wt% H_2 (w/o catalyst)	7.6	5.6	10.4	5.6	7.3	6.5	8.2
Volumetric density (g/L) (w/o catalyst)	112	92	101	71	99		107 (estimated)
Demonstrated reversible wt% H_2 (with catalyst)	6.5	~5	9.3	5.2	4.9 (PCT)	6.1 (TGA)	6.6 (PCT)
Desorp. Temp (°C) (with catalyst)	150-250 (low P)	100-160	200~450 vacuum	100~250	160-300	100~240	160-240
Adsorp. Temp (°C) (with catalyst)	150	120	170-255	100~200	200-300	200-300	160-300
Isothermal Plateau Pressure, with catalyst, (Bar) (temp °C)	1 (280)	1st step 1(~40) 10 (~90)	0.2 (230°C) 1.0 (255°C)	46 (200 °C)	1 (255°C) 60 (375°C)	TBD	1, and 20 (240 °C)
Kinetics (with catalyst)	moderate	Good	Good	Good	TBD	TBD	TBD

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Future Directions

FY 2008:

➢ Complete quantitative characterizations of the release of NH_3 during dehydrogenation from $Li_3AlH_6/3LiNH_2$, and LiMgN.

➢ Continue PCT studies of plateau pressures and the kinetics of hydrogenation and dehydrogenation for LiMgN and $Li_3AlH_6/3LiNH_2$,

➢ Continue to study the reaction mechanisms with XRD, FTIR, NMR.

➢ Begin catalyst studies to improve kinetic performance of materials

➢ Begin studies of $2LiNH_2 + C = Li_2CN_2 + 2H_2$ (rxn. predicted by Theory Group)

➢ Perform cycling studies of the LiMgN system

➢ Use CVS approach to make catalyzed nano Al for regeneration of AlH_3,

➢ Continue explore new materials using high pressure high energy ball milling

FY 2009:

➢ Continue to explore new materials, catalysts

➢ Explore techniques (thermal, chemical) to minimize NH_3 release

➢ Continue to study cycle stabilities

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